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㉙ **Heat-shrinkable laminated film and process for producing the same.**

㉚ Disclosed herein is a heat-shrinkable laminated film comprising at least two layers of a mixed resin layer (A) consisting essentially of 65 to 85 wt% of a polyamide resin and 15 to 35 wt% of a saponified ethylene-vinyl acetate copolymer, and a layer (B) containing at least 55 wt% of a saponified ethylene-vinyl acetate copolymer, the thickness of said layer (A) being larger than that of said layer (B).

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## Description

## Heat-Shrinkable Laminated Film and Process for Producing the same

The present invention relates to a heat-shrinkable laminated film comprising a layer that is mixed resin layer of a polyamide resin (hereinafter referred to as "Ny resin") and a saponified ethylene-vinyl acetate copolymer (hereinafter referred to as "EVOH resin"). More particularly, the present invention relates to a heat-shrinkable laminated film comprising at least two layers of a mixed resin layer (A) consisting essentially of 65 to 85 wt% of an Ny resin and 15 to 35 wt% of an EVOH resin and a layer (B) containing at least 55 wt% of an EVOH resin, the thickness of the layer (A) being larger than that of the layer (B), and a process for producing the heat-shrinkable laminated film.

Most fatty foods such as raw or processed meats have irregular shape and non-uniform size. Frequently, they are shrink-packaged using heat-shrinkable film. A normal method comprises inserting the meat or other object into a bag of the film, removing the air from the bag under vacuum, sealing the opening of the bag, and heating the bag so as to heat-shrink the film into close contact of the film with the object. The heat-treatment may also serve to sterilise the object and is ordinarily carried out at a temperature of 80 to 100°C.

The film used for such shrink packaging needs to have good gas-barrier property and conformable adhesiveness, and needs to be sufficiently shrunk when heated with hot water or hot air at 80 to 100°C. An EVOH resin film can have a high gas-barrier property and can be used for shrink packaging but has rather poor low-temperature stretchability and so is unsuitable for practical use.

Various attempts at eliminating this defect have been proposed. Examples are a heat-shrinkable film having a mixed resin layer of an EVOH resin and a Ny resin (Japanese patent application laid-open (KOKAI) Nos.54-16576 (1979) and 58-36412 (1983)), a heat-shrinkable laminated film composed of an EVOH resin layer and a Ny resin layer (Japanese patent application laid-open (KOKAI) No.56-136365 (1981)), and a heat-shrinkable film comprising a mixed resin layer of an EVOH resin and a Ny resin, and a thermoplastic resin layer laminated on the mixed resin layer so as to provide a heat-sealing property (Japanese patent application laid-open (KOKAI) No.56-15326 (1981)).

However, a film having a barrier layer of a mixture of an EVOH resin and a Ny resin may have a gas permeability that is too high and/or stretchability that is less than is desired.

Accordingly, a film having a layer containing an EVOH resin as the main constituent and showing both high gas-barrier property and excellent stretching film-forming property is now in demand.

It has been found that a heat-shrinkable laminated film having both high gas-barrier property and excellent stretching film-forming property is obtained by laminating a layer containing an EVOH resin with a mixed resin layer of an EVOH resin and a Ny resin, and more particularly, by laminating a resin layer comprising an EVOH resin and a Ny resin at a specific mixing ratio and having a thickness larger than a layer containing an EVOH resin with the layer containing an EVOH resin and the thus obtained laminate is easy to orient.

A heat-shrinkable laminated film according to the present invention comprises at least two layers of a mixed resin layer (A) of 65 to 85 wt% of a Ny resin and 15 to 35 wt% of an EVOH resin, and a layer (B) containing at least 55 wt% of an EVOH resin, a thickness of the layer being larger than that of the layer (B).

In a first aspect of the present invention, there is provided a heat-shrinkable laminated film comprising at least two layers of a mixed resin layer (A) consisting essentially of 65 to 85 wt% of a polyamide resin and 15 to 35 wt% of a saponified ethylene-vinyl acetate copolymer, and a layer (B) containing at least 55 wt% of a saponified ethylene-vinyl acetate copolymer, the thickness of said layer (A) being larger than that of said layer (B).

In a second aspect of the present invention, there is provided a process for producing a heat-shrinkable laminated film comprising laminating at least two layers of a mixed resin layer (A) consisting essentially of 65 to 85 wt% of a polyamide resin and 15 to 35 wt% of a saponified ethylene-vinyl acetate copolymer, and a layer (B) containing at least 55 wt% of a saponified ethylene-vinyl acetate copolymer in a circular die so that the thickness of said layer (A) is larger than that of said layer (B); coextruding the laminate into a tubular shape; and biaxially stretching the tubular laminate to 1.3 to 3.5 times in the machine and transverse directions, respectively, while heating said laminate to 75°C and not higher than 100°C.

An EVOH resin used for the layers (A) and (B) in the heat-shrinkable laminated film of the present invention is a resin of a partially saponified ethylene-vinyl acetate copolymer. The ethylene content in the EVOH resin is preferably 25 to 49 mol%, preferably 30 to 45 mol%, and the saponification degree is preferably not less than 95 mol%. If the ethylene content exceeds 49 mol%, the gas-barrier property may become inferior, while if the ethylene content is less than 25 mol%, the stretching film-forming property may become inferior.

The EVOH resins for the layers (A) and (B) may be either the same or different.

The crystalline melting point of the Ny resin is preferably not higher than 240°C. If the crystalline melting point of the Ny resin exceeds 240°C, when the resin is mixed with an EVOH resin, cross-linking reaction is apt to be produced during the extrusion of the mixed resin layer, thereby tending to produce a gel.

The crystalline melting point is a temperature which shows the maximum value of the melting point curve obtained by measuring with a temperature when elevating 8 mg of a sample at a rate of 8°C/min by using a differential scanning type calorimeter (Mettler Ltd., TA-3000).

As the Ny resin used in the present invention, nylon 6, nylon 11, nylon 12, nylon 6,9, nylon 6,10, nylon 6,12, nylon 6-12, nylon 6-66, etc. are preferable. Among these, nylon 6-66 is most preferable.

The layer (A) composed of a mixed resin of 65 to 85 wt% of a Ny resin and 15 to 35 wt% of an EVOH resin, preferably a mixed resin of 70 to 80 wt% of a Ny resin and 20 to 30 wt% of an EVOH resin. If the Ny resin exceeds 85 wt%, the stretching film-forming property is deteriorated (the inner pressure of the tubular film is raised during inflation or the slipperiness between the dimension guide roll and the film is deteriorated, resulting in nonuniformity in the film width). If the Ny resin is less than 65 wt%, necking is apt to be produced and the stretching film-forming property is deteriorated, resulting in an inferior external appearance of the film. 5

The layer (B) comprises a resin containing at least 55 wt% of an EVOH resin. The layer (B) may be either a layer of an EVOH resin solely, or a layer composed of not less than 55 wt% and less than 100 wt% of an EVOH resin and more than 0 and not more than 45 wt% of at least one resin selected from the group consisting of elastomers such as a polyester elastomer (e.g., a block copolymer-type thermoplastic polyester elastomer) and a polyamide elastomer (a polyester amide elastomer and a polyether amide elastomer), an polyolefin resin such as an ethylene-vinyl acetate copolymer, a saponified ethylene-vinyl acetate copolymer (having a saponification degree of less than 95%) and a polyamide resin which is mixed with the EVOH resin so as to improve the stretching film-forming property, the low-temperature resistance and the flexibility. As such a polyamide resin, nylon 6, nylon 11, nylon 12, nylon 6,9, nylon 6,10, nylon 6,12 and a copolyamide resin: nylon 6-12, and nylon 6-66 are exemplified. As the resin mixed with the EVOH resin, a polyamide resin or a polyester elastomer is preferable. If the EVOH resin is less than 55 wt%, the gas-barrier property is unfavorably insufficient. 10 15

A heat-shrinkable laminated film of the present invention comprises at least the layer (A) and the layer (B), and the numbers of the layers (A) and (B) each may be two or more. When the layers (A) and (B) constituting the laminated film are respectively two or more, the resin composition of each layer may be either the same or different. However, in view of workability, it is preferable that the laminated film comprises one layer (A) and one layer (B). 20

It is necessary that the thickness of the layer (A) is larger than that of the layer (B) in the laminated film of the present invention. If the layers (A) and (B) constituting the laminated film are respectively two or more, it is necessary that the total thickness of the layers (A) is larger than the total thickness of the layers (B). If the thickness of the layer (A) is smaller than that of the layer (B), the stretching property of the film is deteriorated. The thickness of the layer (A) is preferably 1.2 to 3 times as large as that of the layer (B). 25

The laminated film of the present invention requires at least two layers of the layer (A) and the layer (B), and it is possible to laminate another thermoplastic resin layer thereon in order to provide the film with various properties. As the thermoplastic resin, an olefin resin is preferable in view of the extrusion property, stretching film-forming property and sealing property. 30

As the olefin resin are preferable a copolymer of ethylene and a vinyl ester monomer such as an ethylene-vinyl acetate copolymer (hereinafter referred to as "EVA"); a copolymer of ethylene and a monomer selected from the group consisting of an aliphatic unsaturated carboxylic acid and an aliphatic unsaturated carboxylate, e.g., a copolymer of ethylene and a monomer selected from the group consisting of acrylic acid, acrylate, methacrylic acid and methacrylate; an ionomer resin; a mixed resin of a linear low-density polyethylene (hereinafter referred to as "LLDPE") and an EVA; a very low-density polyethylene having a density of not more than 0.91 and a Vicat softening point (measured by ASTM D-1525) of not more than 90°C, preferably not more than 80°C (hereinafter referred to as "VLDPE"); and a mixed resin of VLDPE and a small amount of LLDPE. As the EVA, those containing 3 to 19 wt% of vinyl acetate are preferable. In a mixed resin of an LLDPE and an EVA, the content of the EVA is preferably at least 55 wt% from the viewpoint of the stretching film-forming property. As the LLDPE, a copolymer of ethylene with a small amount of an  $\alpha$ -olefin having 4 to 18 carbon atoms such as butene-1, penten-1, 4-methyl-penten-1, hexene-1 and octene-1, which has a crystalline melting point of 118 to 130°C is preferable. As the ionomer resin, an ion cross-linked polymer is obtained by neutralizing a part of the anions of a copolymer of an  $\alpha$ -olefin such as ethylene and propylene with a partially saponified polymer of an unsaturated carboxylic acid or unsaturated carboxylate such as acrylic acid, methacrylic acid and maleic acid, with metal ions such as Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> and Zn<sup>2+</sup>. As the metal ions, Na<sup>+</sup> and Zn<sup>2+</sup> are generally used. An ionomer resin partially neutralized with bivalent metal ions and containing a Ny oligomer is also usable. An EVA containing 5 to 9 wt% of vinyl acetate and an ionomer resin are most preferable in view of the extrusion property and the stretching film-forming property. 35 40 45 50

In a laminated film of the present invention, at least one olefin layer can be laminated. If it has two olefin resin layers or more, the olefin resin layers may be the same or different. The olefin resin layer may be disposed either between the layer (A) and the layer (B), or preferably on one side or both sides of the laminated film of the layers (A) and (B). By laminating the olefin resin layer, it is possible to improve the extrusion property and the stretching film-forming property, and to provide the laminated film with an excellent sealing property. It is possible to add an inorganic additive and/or an organic additive such as a thermoplastic resin, an inorganic filler and a pigment to the layer (A), the layer (B) and the olefin resin layer in such a quantity as not to impair the stretching film-forming property and the gas-barrier property. 55

Since the adhesiveness between the layer (A) and the layer (B) is good, no particular adhesive layer is required, but an adhesive layer may be provided, if necessary. In this case, the adhesive layer is preferably disposed between the olefin resin layer and the layer (A) or the layer (B) so as to improve the adhesiveness. 60

As the adhesive, a polyolefin which is modified or polymerized with a carboxylic acid such as fumaric acid and maleic acid is preferable. As examples of the polyolefin, a homopolymer of an olefin such as ethylene and propylene, a copolymer such as an ethylene-vinyl acetate copolymer, an ethylene-acrylate copolymer and an 65

ethylene-methacrylate copolymer, and a mixture thereof which do not impair the transparency are exemplified.

A process for producing a heat-shrinkable laminated film according to the present invention will be described.

A laminate of the layer (A) and the layer (B) is coextruded into a tubular shape so that the thickness of the layer(s) (A) is larger than that of the layer(s) (B) by using a circular die equipped with the same number of extruders as the number of the laminated layers. The thus coextruded tubular laminate is immediately rapidly cooled, and the thus obtained substantially amorphous tubular film is heated. The thus heated film is biaxially stretched to 1.3 to 3.5 times, preferably 1.5 to 3 times in the machine and transverse directions, respectively, by an inflation method, thereby producing a heat-shrinkable film. The heating temperature of the substantially amorphous tubular film is not lower than 75°C and lower than 100°C, preferably 85 to 95°C. If the heating temperature is lower than 75°C, the stretching film-forming property is deteriorated. On the other hand, if the heating temperature is 100°C or higher, it is impossible to obtain the desired heat-shrinkage. It is necessary that a heat-shrinkable film of the present invention has a thermal-shrinkage of not less than 10%, preferably not less than 15% in both machine and transverse directions when the film is immersed in a hot water of 98°C for 1 minute. If the thermal-shrinkage is less than 10%, a wrinkle of the film may be produced on the surface of a package or the close contact between the content and the packaging film is impaired, thereby deteriorating the external appearance of the goods.

A heat-shrinkable laminated film of the present invention consisting of the layer (A) and the layer (B) preferably has a thickness of not more than 30 µm in view of flexibility, and a thickness which restricts the gas permeability to not more than 150 cc/m<sup>2</sup>•day•atm. A heat-shrinkable film of the present invention comprising the layer (A), the layer (B) and a thermoplastic resin layer preferably has a thickness of 15 to 120 µm, and a thickness which restricts the gas permeability to not more than 150 cc/m<sup>2</sup>•day•atm, the total thickness of the layer (A) and the layer (B) being not more than 30 µm, so as to provide the film flexibility.

A heat-shrinkable laminated film of the present invention, which is produced by laminating a layer containing an EVOH resin layer which has a high gas-barrier property on a mixed resin layer of an EVOH resin and a Ny resin which has a relatively high gas-barrier property and good stretching film-forming property in a specific layer-thickness ratio, is a good food packaging film having both high O<sub>2</sub> gas-barrier property and excellent stretching film-forming property.

Since the stretching film-forming property is excellent, it is possible to greatly reduce the dimensional change of the film with time without the need for excessive orientation and the film does not occur any ply separation during a high-temperature treatment in a sterilization and heat shrinkage process. A heat-shrinkable laminated film of the present invention also has a good property of clinging to an article in conformity therewith.

The present invention will be explained more in detail while referring to the following non-limitative examples.

#### Examples 1 to 11, Comparative Examples 1 to 6

Resins shown in Table 1 were separately charged into a circular die by a plurality of extruders, and the laminates having the layer-structures shown in Table 2 were coextruded. Each of the tubular laminates extruded from the die was cooled in a cooling bath of 5 to 20°C, to obtain a substantially amorphous tubular laminate 200 mm in folded width and 60 to 200 µm in thickness. In a heating bath adjusted to the temperature shown in Table 2, the thus obtained tubular laminate was heated for about 6 seconds while feeding to the heating bath at a rate of 20 m/min, and the thus heated tubular laminate was passed through nip rolls of a rotational rate of 20 m/min. The heated tubular laminate was stretched to 2 times in the machine direction (L) at room temperature and stretched in the transverse direction (T) by expanding it 2 times the diameter of the tubular laminate by the air supplied into the tubular laminate by the time the laminate was passed through second nip rolls of a rotational rate of 40 m/min. The thus obtained biaxially oriented film was about 385 mm in folded width and 15 to 50 µm in thickness.

The kinds and physical properties of the resins used in Examples are shown in Table 1, the layer-structures of the laminated films obtained and the results of the tests on the properties of the films are shown in Table 2, and the methods for the tests on the properties are shown in Table 3.

#### Example 12

Resins shown in Table 1 were separately charged into a circular die by a plurality of extruders, and the laminate having the layer-structures shown in Table 2 was coextruded. The tubular laminate extruded from the die was cooled in a cooling bath of 5 to 20°C, to obtain a substantially amorphous tubular laminate 262 mm in folded width and 95 µm in thickness. In a heating bath adjusted to the temperature shown in Table 2, the thus obtained tubular laminate was heated for about 6 seconds while feeding to the heating bath at a rate of 27 m/min, and the thus heated tubular laminate was passed through nip rolls of a rotational rate of 27 m/min. The heated tubular laminate was stretched to 1.5 times in the machine direction (L) at room temperature and stretched in the transverse direction (T) by expanding it 1.5 times the diameter of the tubular laminate by the air supplied into the tubular laminate by the time the laminate was passed through second nip rolls of a rotational rate of 40 m/min. The thus-obtained biaxially oriented film was about 385 mm in folded width and 42 µm in thickness.

The kinds and physical properties of the resins used in Example 12 are shown in Table 1, the layer-structures

of the laminate film obtained and the results of the tests on the properties of the film are shown in Table 2, and the methods for the tests on the properties are shown in Table 3.

#### Example 13

Resins shown in Table 1 were separately charged into a circular die by a plurality of extruders, and the laminate having the layer-structures shown in Table 2 was coextruded. The tubular laminate extruded from the die was cooled in a cooling bath of 5 to 20°C, to obtain a substantially amorphous tubular laminate 133 mm in folded width and 378  $\mu\text{m}$  in thickness. In a heating bath adjusted to the temperature shown in Table 2, the thus obtained tubular film was heated for about 6 seconds while feeding to the heating bath at a rate of 13 m/min, and the thus heated tubular laminate was passed through nip rolls of a rotational rate of 13 m/min. The heated tubular laminate was stretched to 3 times in the machine direction (L) at room temperature and stretched in the transverse direction (T) by expanding it 3 times the diameter of the tubular laminate by the air supplied into the tubular laminate by the time the laminate was passed through second nip rolls of a rotational rate of 40 m/min. The thus-obtained biaxially oriented film was about 385 mm in folded width and 42  $\mu\text{m}$  in thickness.

The kinds and physical properties of the resins used in Example 13 are shown in Table 1, the layer-structures of the laminated film obtained and the results of the tests on the properties of the film are shown in Table 2, and the methods for the tests on the properties are shown in Table 3.

Table 1

Resin	Abbreviation	Physical properties
Nylon 6-66 copolymer	Ny <sup>1</sup>	crystalline melting point (T <sub>m</sub> ): 200°C
Nylon 6-12 copolymer	Ny <sup>2</sup>	crystalline melting point (T <sub>m</sub> ): 130°C
Saponified ethylene-vinyl acetate copolymer	EVOH	saponification degree: 98%, crystalline melting point (T <sub>m</sub> ): 164°C, ethylene content: 44 mol%
Modified saponified ethylene-vinyl acetate	Mod. (EVOH)	blending of EVOH and a polyester elastomer, Nihon Gosei Kagaku K.K. Soanol STS improved
Mixture of ionomer/nylon oligomer	IO/PA	metal ion: Zn <sup>++</sup> , Mitsui Du Pont, Himilan
Ionomer	IO	crystalline melting point (T <sub>m</sub> ): 98°C, metal ion: Na <sup>+</sup> , Mitsui Du Pont, Himilan
Very low-degree polyethylene	VLDPE	crystalline melting point (T <sub>m</sub> ): 115°C, density: 0.900, Sumitomo Kagaku Kogyo K.K., Excelene, Vicat softening point: 75°C
Ethylene- $\alpha$ -olefin copolymer	LLDPE	crystalline melting point (T <sub>m</sub> ): 120°C, Mitsui Sekiyu Kagaku K.K., Ultzex
Ethylene-vinyl acetate copolymer	EVA	vinyl acetate content: 5 wt%, crystalline melting point (T <sub>m</sub> ): 102°C
Carboxylic acid modified ethylene-ethylacrylate	EEA <sup>g</sup> COOH	crystalline melting point (T <sub>m</sub> ): 110°C, blended system containing 15 wt% of ethylacrylate
Ethylene-acrylate based tricopolymer	EEA-MAH	crystalline melting point (T <sub>m</sub> ): 95°C, Sumitomo Kagaku K.K., Bondine

Table 2

Examples & Com- parative Examples	Layer-structure (mixing weight ratio and thickness of layers: $\mu\text{m}$ )	Stretching ratio	Heating tempera- ture (°C)	Stretch- ability	Thermal shrinkage (L/T %)	Dimensional stability	Gas- barrier property (cc/m <sup>2</sup> . day.atm)
Example 1	[Ny <sup>1</sup> /EVOH(7/3)]/EVOH (10) (5)	2 x 2	80	A	26/31	B	139
Example 2	[Ny <sup>1</sup> /EVOH(8/2)]/[Ny <sup>1</sup> /EVOH(3/7)]/ (10) (10) [Ny <sup>1</sup> /EVOH(8/2)] (10)	2 x 2	80	A	29/33	B	66
Example 3	[Ny <sup>1</sup> /EVOH(65/35)]/[EEA <sup>g</sup> COOH/EVOH/ (12) (1) (6) EEA <sup>g</sup> COOH/[LLDPE/EVA(3/7)] (1) (20)	2 x 2	95	B	22/23	B	110
Example 4	[Ny <sup>1</sup> /EVOH(8/2)]/EVOH/EEA <sup>g</sup> COOH/ (12) (6) (1) IO (20)	2 x 2	85	A	24/28	A	105
Example 5	[LLDPE/EVA(3/7)]/[EEA <sup>g</sup> COOH/EVOH/ (5) (1) (10) [Ny <sup>1</sup> /EVOH(8/2)]/EEA <sup>g</sup> COOH/IO (12) (1) (20)	2 x 2	95	A	27/28	A	77
Example 6	EVA/EEA-MAH/EVOH/[Ny <sup>1</sup> /EVOH(7/3)]/ (4) (1) (6) (8) EEA-MAH/IO (1) (25)	2 x 2	95	A	26/28	A	124

Examples & Com- parative Examples	Layer-structure (mixing weight ratio and thickness of layers: $\mu\text{m}$ )	Stretching ratio	Heating tempera- ture (°C)	Stretch- ability	Thermal shrinkage (L/T %)	Dimensional stability	Gas- barrier property (cc/m <sup>2</sup> . day.atm)
Example 7	[Ny <sup>1</sup> /EVOH(85/15)]/EVOH/EEA <sup>g</sup> COOH/ IO (8) (6) (1) (20)	2 x 2	90	B	28/29	A	134
Example 8	EVA/EEA-MAH/Mod.EVOH/[Ny <sup>1</sup> / (4) (1) (6) EVOH(7/3)]/EEA-MAH/IO (8) (1) (22)	2 x 2	95	A	28/29	A	117
Example 9	EVA/EEA <sup>g</sup> COOH/Mod.EVOH/[Ny <sup>1</sup> / (4) (1) (5) EVOH(8/2)]/EEA <sup>g</sup> COOH/VLDPE (9) (1) (22)	2 x 2	95	A	27/29	A	135
Example 10	EVA/EEA <sup>g</sup> COOH/Mod.EVOH/[Ny <sup>1</sup> / (4) (1) (5) EVOH(8/2)]/EEA <sup>g</sup> COOH/VLDPE/LLDPE(9/1)] (9) (1) (22)	2 x 2	95	A	28/28	A	138
Example 11	EVA/EEA <sup>g</sup> COOH/Mod.EVOH/[Ny <sup>1</sup> / (4) (1) (5) EVOH(8/2)]/EEA <sup>g</sup> COOH/(IO/PA) (9) (1) (22)	2 x 2	95	A	26/29	A	136
Example 12	EVA/EEA-MAH/Mod.EVOH/[Ny <sup>2</sup> / (4) (1) (6) EVOH(7/3)]/EEA-MAH/IO (8) (1) (22)	1.5 x 1.5	95	A	22/26	A	120



Examples & Com- parative Examples	Layer-structure (mixing weight ratio and thickness of layers: $\mu\text{m}$ )	Stretching ratio	Heating tempera- ture ( $^{\circ}\text{C}$ )	Stretch- ability	Thermal shrinkage ( $\text{L/T } \%$ )	Dimensional stability	Gas- barrier property ( $\text{cc/m}^2 \cdot$ $\text{day} \cdot \text{atm}$ )
Example 13	EVA/EEA-MAH/Mod.EVOH/[Ny <sup>2</sup> / (4) (1) (6) EVOH(7/3)]/EEA-MAH/IO (8) (1) (22)	3 x 3	95	A	35/35	A	112
Compara- tive Example 1	Ny <sup>1</sup> /EVOH/Ny <sup>1</sup> (10) (10) (10)	2 x 2	80	C	28/32	D	95
Compara- tive Example 2	[Ny <sup>1</sup> /EVOH(7/3)]/EEA <sup>g</sup> COOH/EVOH/ (12) (1) (6) EEA <sup>g</sup> COOH/[LLDPE/EVA(3/7)] (1) (20)	2 x 2	95	C	30/36	D	132
Compara- tive Example 3	[Ny <sup>1</sup> /EVOH(8/2)]/EEA <sup>g</sup> COOH/EVOH/ (6) (1) (8) EEA <sup>g</sup> COOH/IO (1) (20)	2 x 2	95	C	31/35	C	101
Compara- tive Example 4	[Ny <sup>1</sup> /EVOH(65/35)]/EVA (30) (15)	2 x 2	95	B	32/33	C	175
Compara- tive Example 5	[Ny <sup>1</sup> /EVOH(6/4)]/EEA <sup>g</sup> COOH/IO (15) (1) (20)	2 x 2	95	C	30/31	C	165

Examples & Comparative Examples	Layer-structure (mixing weight ratio and thickness of layers: $\mu\text{m}$ )	Stretching ratio	Heating tempera- ture ( $^{\circ}\text{C}$ )	Stretch- ability	Thermal shrinkage ( $\text{L/T } \%$ )	Dimensional stability	Gas- barrier property ( $\text{cc}/\text{m}^2 \cdot$ $\text{day} \cdot \text{atm}$ )
Compara- tive Example 6	$\text{Ny}^1/\text{EVOH}(3/7)/\text{IO}$ (10) (20)	2 x 2	-	D	-	-	-

Table 3

Property	Method for testing the property	5
1. Thermal-shrinkage	20 pieces of 10 cm x 10 cm film were immersed into a hot bath of 98°C in a loose state. The heat-shrinkage was represented by the average value of the ratios of the longitudinal and transverse lengths of the films to the respective original lengths.	10 15
2. Stretchability	A: Very good. B: Good. C: Stretchable but impracticable due to the production of a small necking and nonuniformity in film thickness. D: Difficult to stretch.	20 25
3. Gas-barrier property	Represented by the amount of oxygen transmitted through the film at 30°C and 100% RH. A high gas-barrier film is required to have a value of not more than 150 cc/m <sup>2</sup> ·day·atm.	30
4. Dimensional stability	The dimensional change of a stretched film of about 1 m long left to stand at 23°C and 50% RH for 2 weeks was measured. A: Less than 5 % (Practicable). B: Not less than 5 and less than 8% (Practicable). C: 8 to 10% (Impracticable). D: More than 10% (Impracticable).	35 40 45

**Claims**

1. A heat-shrinkable laminated film comprising at least two layers including a layer (A) comprising a blend of polyamide resin and a saponified ethylene-vinyl acetate polymer characterised in that the blend comprises 65 to 85 wt% of a polyamide resin and 15 to 35 wt% of a saponified ethylene-vinyl acetate copolymer, and the laminate also includes a layer (B) containing at least 55 wt% of a saponified ethylene-vinyl acetate copolymer, the thickness of said layer (A) being larger than that of said layer (B).

2. A heat-shrinkable laminated film according to claim 1, wherein said layer (B) is a layer of a saponified ethylene-vinyl acetate copolymer.

3. A heat-shrinkable laminated film according to claim 1, wherein said layer (B) is a mixed resin layer consisting essentially of not less than 55 wt% and less than 100 wt% of a saponified ethylene-vinyl acetate copolymer and more than 0 and not more than 45 wt% of at least one resin selected from the

group consisting of a polyester elastomer, a polyamide elastomer, a polyolefin resin and a polyamide resin.

4. A heat-shrinkable laminated film according to claim 3, wherein the polyester elastomer is a block copolymer-type thermoplastic polyester elastomer, the polyamide elastomer is a polyester amide elastomer or polyether amide elastomer, the polyolefin resin is an ethylene-vinyl acetate copolymer or a saponified ethylene-vinyl acetate copolymer having a saponification degree of less than 95%, and the polyamide resin is nylon 6, nylon 11, nylon 12, nylon 6,9, nylon 6,10, nylon 6,12, nylon 6-12 or nylon 6-66.

5. A heat-shrinkable laminated film according to claim 1, the polyamide resin is one of the crystalline melting point of not higher than 240°C.

6. A heat-shrinkable laminated film according to claim 5, the polyamide resin is nylon 6, nylon 11, nylon 12, nylon 6,9, nylon 6,10, nylon 6,12, nylon 6-12 or nylon 6-66.

7. A heat-shrinkable laminated film according to claim 1, the ethylene content of the saponified ethylene-vinyl acetate copolymer is 25 to 49% and the saponification degree of the saponified ethylene-vinyl acetate copolymer is not less than 95 mol%.

8. A heat-shrinkable laminated film according to claim 1, the thickness of the layer (A) is 1, 2 to 3 times as large as that of the layer (B).

9. A heat-shrinkable laminated film according to claim 1, further comprising at least one olefin resin layer, and an adhesive layer disposed at least between said olefin layer and said layer (A) or said layer (B).

10. A heat-shrinkable laminated film according to claim 1 or 9, wherein the thickness of the layer (A) and the layer (B) is not more than 30  $\mu\text{m}$  and a thickness in which the gas permeability is not more than 150  $\text{cc}/\text{m}^2 \cdot \text{day} \cdot \text{atm}$ .

11. A heat-shrinkable laminated film according to claim 9, said olefin resin is a copolymer of ethylene and a vinyl ester monomer, a copolymer of ethylene and a monomer selected from the group consisting of an aliphatic unsaturated carboxylic acid and an aliphatic unsaturated carboxylate, a copolymer of ethylene and a monomer selected from the group consisting of acrylic acid, acrylate, methacrylic acid and methacrylate, an ionomer resin, a mixed resin of a linear low-density polyethylene and a copolymer of ethylene and vinyl acetate, a very low-density polyethylene, and a mixed resin of a very low-density polyethylene or a small amount of a linear low-density polyethylene.

12. A heat-shrinkable laminated film according to claim 9, said adhesive is a polyolefin modified or polymerized with a carboxylic acid.

13. A heat-shrinkable laminated film according to claim 9, the thickness of the laminated film is 15 to 120  $\mu\text{m}$  and a thickness in which the gas permeability is not more than 150  $\text{cc}/\text{m}^2 \cdot \text{day} \cdot \text{atm}$ .

14. A process for producing a heat-shrinkable laminated film comprising laminating at least two layers of a mixed resin layer (A) consisting essentially of 65 to 85 wt% of a polyamide resin and 15 to 35 wt% of a saponified ethylene-vinyl acetate copolymer, and a layer (B) containing at least 55 wt% of a saponified ethylene-vinyl acetate copolymer in a circular die so that the thickness of said layer (A) is larger than that of said layer (B); coextruding the laminate into a tubular shape; and biaxially stretching the tubular laminate to 1.3 to 3.5 times in the machine and transverse directions, respectively, while heating said laminate to 75°C and not higher than 100°C.

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54 **Heat-shrinkable laminated film and process for producing the same.**

57 Disclosed herein is a heat-shrinkable laminated film comprising at least two layers of a mixed resin layer (A) consisting essentially of 65 to 85 wt% of a polyamide resin and 15 to 35 wt% of a saponified ethylene-vinyl acetate copolymer, and a layer (B) containing at least 55 wt% of a saponified ethylene-vinyl acetate copolymer, the thickness of said layer (A) being larger than that of said layer (B).

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# EUROPEAN SEARCH REPORT

Application Number

EP 88 30 0984

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X	EP-A-0 132 565 (ALLIED CORP.) * Page 5, line 37 - page 6, line 7; page 6, lines 16-20,32-34; page 7, lines 10-12; page 3, line 24 - page 4, line 2; page 4, lines 36,38; page 5, lines 9-11,22-33 * ---	1,2,5,7 ,9,11, 14	B 32 B 27/08
X	EP-A-0 064 330 (AMERICAN CAN CO.) * Page 4, lines 17-25; page 7, lines 12-18,22-25; page 8, lines 3-9; page 9, lines 8-14; page 14, lines 1-18; page 15, lines 5-8; page 18, lines 6-9 * ---	1,2,5,6 ,7,9,10 ,12	
X	GB-A-1 591 424 (W.R. GRACE & Co.) * Page 2, lines 115-127; page 3, lines 24-42,80-88; page 4, lines 6-50,66,67,79-88 * -----	1-3,5,6 ,7,9,11 ,12	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 24-01-1989	Examiner IBARROLA TORRES O.M.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

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